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**"Process for producing surface-modified workpieces"**

5 The present invention relates to processes for producing surface-modified workpieces made from metal and/or one or more alloys, to the workpieces produced by means of these processes and to processes for joining at least two such workpieces.

10 The direct coating of aluminum or aluminum alloys by means of organic coating systems is virtually impossible on account of the inadequate bonding of the organic coating systems to the aluminum. Therefore, to improve the bonding between the starting material and  
15 organic coating systems, it is known to subject aluminum or aluminum alloys to what is known as a boehmite treatment, in which hot water or hot steam, if appropriate together with ammonia or amines, is brought into contact with the workpiece, so as to form or  
20 thicken an aluminum oxide or boehmite layer. This then allows an organic coating to be applied. EP 1 142 663 A1 describes boehmite processes, in which deionized water at temperatures of approximately 100°C or steam at temperatures of 150°C is used to surface-modify  
25 aluminum parts. US 3,945,899 has disclosed a boehmite treatment of aluminum parts with water at a temperature of from 65 to 100°C or steam at temperatures of 100 to 180°C, with the addition of amines and ammonia further boosting the aluminum oxide layer.

30 It is also known from this document to subject aluminum or its alloys to a chemical surface treatment using aqueous solutions of chromates or phosphates, in order in this way firstly to increase the bonding and  
35 secondly to reduce the susceptibility to corrosion. This conversion treatment, as it is known, is also known from Stolzenfels (Industrie-Lackierbetrieb,

[Industrial coating operation] No. 3, pp. 93-98, Curt R. Vincentz Verlag), which describes chromating treatments of aluminum workpieces at temperatures of from 20 to 50°C. Riese-Meyer et al. (Aluminium 1991, No. 12, pages 1215-1221) describes chemical conversion treatments by means of layer-forming phosphating steps and chromating steps, allowing the coating bonding and corrosion resistance of aluminum workpieces to be improved. According to this document too, the chromating is carried out at a temperature of from 20 to 30°C or 30 to 40°C.

However, the abovementioned processes have proven disadvantageous inter alia on account of energy considerations. Since the workpieces which are to be modified in accordance with the prior art are generally at room temperature, i.e. are used in a cooled state with respect to a preceding brazing or joining process, considerable handling and time are required for the surface modification of such workpieces. Moreover, the shaped bodies made from aluminum or aluminum alloys which are to be modified in the prior art tend toward what is known as coarse-grain formation, on account of the slow cooling process carried out after they have been produced.

Therefore, the present invention is based on the technical problem of providing processes which overcome the abovementioned drawbacks, in particular of providing processes which provide workpieces made from aluminum or aluminum alloys with improved bonding and/or corrosion resistance at lower cost, in particular workpieces whose structure is distinguished by reduced coarse-grain formation compared to conventionally produced aluminum or aluminum alloy workpieces while having a corrosion resistance and bonding which are as good if not better.

The present invention solves the technical problem on

which it is based by providing a process for producing surface-modified workpieces made from aluminum or one or more aluminum alloys, comprising the steps of providing the workpiece which is to be modified and is  
5 at a temperature of from 40 to 700°C, preferably 80 to 550°, in particular 300 to 550°C, and then treating this workpiece at the abovementioned temperature with at least one modifying agent to obtain the surface-modified workpiece, the at least one modifying agent  
10 being at a temperature of from -200°C to 100°C, preferably at most 80°C and in particular at least 0°C, preferably 20 to 65°C. Therefore, the invention solves the problem on which it is based in particular by providing, at a relatively high temperature, a  
15 workpiece whose surface is to be modified and bringing it into contact with at least one modifying agent which is at a lower temperature, so as produce a surface-modified workpiece.

20 In the context of the present invention, a workpiece is to be understood as meaning an object of any desired form which, by way of example, may be in the form of a shaped body, i.e. a body of defined form, or alternatively also in the form of granules or a powder.  
25 In a preferred embodiment, the workpiece is in the form of a heat exchanger or a significant component thereof.

In a preferred embodiment of the present invention, the workpiece which is to be modified is composed of  
30 aluminum, magnesium, copper or one or more aluminum and/or magnesium and/or copper alloys, i.e. it consists of aluminum or one or more alloys or it substantially comprises aluminum or one or more aluminum alloys, for example, in amounts of at least 50, 60, 70, 80, 90, 95  
35 and in particular 99% by weight, based on the weight of the workpiece.

In its first configuration, the invention provides for the workpiece whose surface is to be modified to be

provided in heated form, the workpiece to be modified being at a temperature of from 40 to 700°C, in particular 100 to 550°C, preferably 150 to 550° and particularly preferably 300 to 550°C. In a preferred  
5 embodiment, this can be achieved by virtue of the fact that the workpiece is used according to the invention when it is still hot immediately following its production process, e.g. after it emerges from a brazing zone, after thermal joining processes or after  
10 heating in chamber furnaces, so as to exploit the heat capacity which is present in these workpieces. The workpiece which is at one of the abovementioned temperatures, for example a temperature of from 80 to 550, in particular 300 to 550°C, is consequently  
15 treated by utilizing its existing elevated temperature, i.e. by being brought into contact with at least one surface-modifying agent, in such a way as to achieve the desired surface modification of the workpiece.

20 The surface modification which is desired in accordance with the invention is in this case a chemical conversion, i.e. the formation of a conversion layer and/or the formation or thickening of a boehmite layer or aluminum oxide layer. In a preferred embodiment, the  
25 surface modification which is desired in accordance with the invention may also comprise the incorporation of corrosion-inhibiting substances into the aluminum oxide or boehmite layer and/or the production of conversion layers by chemical-physical modification of  
30 possibly existing flux layers.

For example, it is possible to provide for workpieces which already include a CAB flux layer on account of a preceding CAB brazing process to be treated by means of  
35 the procedure according to the invention in such a way that the existing CAB flux layer is chemically-physically modified. The procedure according to the invention may result in the existing flux layer being doped, for example with metals from main groups I, II,

III or IV or from the transition groups, in particular IV to VI, and/or having its oxygen content increased. The treatment according to the invention results, inter alia, in an improved resistance to corrosion.

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The use of a modifying agent at a low temperature, in particular a temperature from  $-200^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , preferably 0 to  $80^{\circ}\text{C}$ , particularly preferably 20 to  $65^{\circ}\text{C}$ , which is preferred in accordance with the invention leads, when treating a workpiece at a high temperature of from 80 to  $700^{\circ}\text{C}$ , in particular 300 to  $550^{\circ}\text{C}$ , to rapid cooling of the workpiece and therefore advantageously to prevention or reduction of the coarse-grain formation in the workpiece. Consequently, the resulting workpieces under certain circumstances advantageously differ in terms of their structure from conventionally produced workpieces.

The treatment of flux (CAB)-coated workpieces which is preferably provided in accordance with the invention under certain circumstances leads to an advantageous scaly, continuous and rounded appearance of the flux layer of the aluminum part, which differs from the open-pore, sharp-edged and platelet-like appearance of untreated flux-coated aluminum parts.

In a further configuration of the present invention, the present technical problem is solved by providing a process for producing surface-modified workpieces made from a metal and/or one or more alloys, comprising the steps of providing the workpiece that is to be modified and treating this workpiece with at least one modifying agent to obtain a surface-modified workpiece, the at least one modifying agent being at a temperature of from 80 to  $550^{\circ}\text{C}$ , preferably 100 to  $200^{\circ}\text{C}$ , preferably 150 to  $200^{\circ}\text{C}$ .

In this configuration of the invention, the workpiece which is to be modified may be at a temperature of from

15 to 80°C, in particular 40 to 65°C, but also 20 to 60°C, in particular 20 to 40°C, preferably 20 to 30°C, or from 80 to 700°C, preferably 100 to 700°C, preferably 150 to 700°C, in particular 300 to 550°C.

5 This configuration of the present invention also allows the advantageous surface-modification of a workpiece, in particular the production of a metal oxide or boehmite layer, the thickening of an existing metal oxide or boehmite layer, the incorporation of  
10 corrosion-inhibiting substances into a metal oxide or boehmite layer and/or the production of conversion layers by chemical-physical modification, in particular of flux layers.

15 Following the surface modification of the workpiece, the workpieces can be treated further in the usual way, in particular by being rinsed and dried. Of course, it is also possible to carry out a further coating operation, for example by means of organic coating  
20 systems. The present process therefore provides part of the production process of a workpiece, for example a heat exchanger. The procedure which is provided for in accordance with the invention, within this production process, leads to a reduction in the production costs  
25 for workpieces, to a saving on energy and resources, in particular by utilizing existing heat capacities of the workpieces, and to the reduced use or the avoidance of the use of aggressive chemicals for the surface treatment.

30 Under certain circumstances, all known chemical elements, compounds, mixtures or other compositions may be suitable for use as the modifying agent. A modifying agent which is preferably used is one or more  
35 compounds, in particular one or more metal salts of one or more elements from the transition groups of the PSE, in particular transition groups IV to VI of the PSE (periodic system of the elements), for example titanium, hafnium, vanadium, tantalum, molybdenum,

tungsten and in particular zirconium.

In a further embodiment of the present invention, the modifying agent may be one or more compounds, in particular one or more metal salts of one or more elements from main groups I, II, III, and/or IV of the periodic system of the elements, for example a metal salt of beryllium, barium, in particular of magnesium or calcium or sodium or potassium.

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In a further embodiment of the present invention, the modifying agent may be one or more compounds of one or more elements from main groups V, VI, VII and/or VIII of the periodic system of the elements.

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In a preferred embodiment of the invention, the abovementioned metals may be in salt form with anions selected from the group consisting of chlorides, carbonates, in particular hydrogen carbonates, nitrates, sulfates, peroxides and phosphates. In particular the metal salts of elements from main groups I and II, for example potassium, sodium and calcium, may be in the form of a hydroxide solution, i.e. KOH, NaOH or  $\text{Ca}(\text{OH})_2$ , or in the form of a borate, aluminate, silicate or halide, in particular fluoride.

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In a further preferred embodiment of the invention, the at least one modifying agent is a CAB-flux ("controlled atmosphere brazing") of the general formula  $\text{K}_x\text{AlF}_y$  where x equals 1 to 3 and y = 4 to 6, for example potassium aluminum hexafluoride and/or  $\text{Cs}_x\text{AlF}_y$ .

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In a further preferred embodiment, the modifying agent used is an ammonium salt, such as for example ammonium fluoride or ammonium carbonate, potassium fluoride, sodium or potassium silicate, sodium or potassium borate, sodium or potassium aluminate, crosslinkable, in particular organometal, such as for example organozirconium or organotitanium, or organosilicon

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compounds, or alternatively hydrogen peroxide.

In a particularly preferred embodiment, the CAB flux, ammonium salt and/or potassium fluoride are used in alkaline phase, in particular in the form of aqueous, preferably alkaline solutions or alkaline vapors or aerosols, to treat the workpiece.

The metal compounds of one of the elements of the transition groups, in particular transition groups IV to VI, or main groups I, II, III or IV, may be in organic and/or inorganic phase, preferably in aqueous phase, in particular in liquid or gaseous phase, preferably in aerosol form or as a vapor. The water which is used for the dissolution is preferably deionized water.

In a further preferred embodiment, there is provision for water, preferably deionized and distilled water, to be used as modifying agent for treating the surface of the workpiece. Of course, according to the invention it is also possible for the surface-modifying agent used to be aqueous solutions of ammonia, of amines, in particular primary, secondary or tertiary amines, for example mono-, di- or triethanolamines, dimethylethanolamines, organic acids or salts of ammonia, amines, halogenated organic compounds and/or organic acids. Of course, it is also possible to use mixtures of the abovementioned modifying agents.

It is preferable to use a solution of 0.1 - 1% of KOH and/or 0.1 - 1% of  $\text{NH}_4\text{OH}$  and/or 0.1 - 1% of  $\text{K}_x\text{AlF}_y$  ( $x = 1$  to  $3$ ,  $y = 4$  to  $6$ ) and/or 0.1 - 1% of  $\text{Ca}(\text{NO}_3)_2$  and/or 0.1 - 1% of salts of the elements of transition groups IV to VI of the PSE in deionized water.

In a particularly preferred embodiment of the present invention, the starting workpiece used for the process according to the invention is a CAB flux-coated



workpiece which results from a CAB brazing process and is treated, under the conditions mentioned above, with one or more of the modifying agents used. In particular if the surface is treated with water or aqueous solutions, it is possible to obtain a modified surface with an increased oxygen content; depending on the type of modifying agent used, this surface may also be doped, for example with one or more of the metals from main group I, II, III or IV or from the transition groups, in particular transition groups IV to VI, or other modifying agents used.

In another preferred embodiment, the invention provides for the metal salt, the CAB flux, ammonium salt and/or potassium fluoride or another constituent of the modifying agent to be used in a matrix, for example a matrix of organic and/or inorganic solvents or mixtures thereof, to treat the surface of the workpiece. In this case, the matrix contains organometal, in particular organosilicon compounds. In particular, the matrix contains organic and/or inorganic polymers, or alternatively a mixture of the abovementioned substances.

In a particularly preferred embodiment, there is provision for the metal salt, the CAB flux, ammonium fluoride and/or potassium fluoride or another constituent of the modifying agent to be used in a concentration of from 10 ppm to 100000 ppm, preferably from 50 ppm to 10 000 ppm in the treatment.

The at least one modifying agent is preferably brought into contact with the workpiece that is to be modified by the workpiece being immersed in the at least one agent and impregnated with the agent or by it being rinsed or flooded with the at least one modifying agent and thus impregnated with it, or by the at least one modifying agent being sprayed onto the workpiece, in particular by means of what is known as airless or

ultrasound atomization, or being brought into contact with it is some other form.

In a particular embodiment, it is possible to provide for the modifying agent to act on the workpiece at a pressure which is higher than atmospheric pressure. In the case of spraying, in addition to compressed air it is also possible to use other gases, for example oxygen, nitrogen, fluorine, ozone or steam.

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Examples of metal salts used include aqueous solutions of  $\text{Ca}(\text{NO}_3)_2$  or  $\text{Zr}(\text{NO}_3)_4$ , in particular in concentrations of between 0.1% and 5%, the pH of which is preferably between 5.5 and 7.5 to 8. The temperature of use is in this case advantageously between 40°C and 60°C. Under certain circumstances, it may also be advantageous to add from 0.005% to 5% of tetraethylammonium tetrafluoroborate.

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20 A solution of this type is used in particular to treat a brazed, preferably CAB-brazed, heat exchanger.

According to an advantageous embodiment, the at least one modifying agent includes a biocidal agent. By way of example, it is desirable for a heat exchanger used in a heating and/or air-conditioning installation to have a germ-inhibiting action which is produced as a result.

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According to a further advantageous embodiment, the modifying agent produces an oxidation-inhibiting action by virtue of the agent including an oxidation inhibitor or producing an oxidation inhibitor on the surface by means of the process according to the invention. An oxidation inhibitor is provided, for example, by a metal oxide or boehmite layer.

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Of course, the invention also relates to surface-modified workpieces produced by means of the

abovementioned processes, in particular surface-modified heat exchangers made from aluminum or aluminum alloys.

- 5 In an advantageous refinement of the invention, in a further step the surface-modified workpiece is provided with one or more organic or inorganic coating systems which particularly advantageously has germ-inhibiting and/or hydrophilic or hydrophobic properties. It is  
10 possible for these coating layers to be applied with or without an intervening drying step.

- The invention is also implemented by a process for joining two or more workpieces as claimed in claim 24.  
15 A production process which includes a process of this type can be carried out quickly, so that it is possible to reduce the manufacturing costs. This applies in particular to processes for cohesively joining a plurality of workpieces, but is also achieved in other  
20 joining processes, such as for example mechanical joining, in which case under certain circumstances it may be necessary to (re)heat the workpiece in order to apply the process according to the invention.

- 25 The invention is also achieved by an apparatus for cohesively joining at least two workpieces, in which a temperature-control chamber for controlling the temperature of, in particular heating, the workpieces, has a device for applying a surface-modifying agent to  
30 at least one of the workpieces. The temperature-control chamber advantageously serves simultaneously for cohesive bonding, such as for example brazing or soldering or welding, and surface-modifying the workpieces.

- 35 The device for applying a surface-modifying agent is preferably designed as a spray nozzle, the temperature of which can itself particularly preferably be controlled in order for the process according to the

invention to be carried out. It is equally possible for the temperature of the surface-modifying agent to be controlled in a feedline of the device.

- 5 Otherwise, the apparatus according to the invention may under certain circumstances be constructed in a known way, for example as a vacuum or continuous brazing furnace.
- 10 Further advantageous configurations of the present invention will emerge from the subclaims.